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Title: High Performing and Durable Pyrophosphate Based Composite Membranes
for Intermediate Temperature Fuel Cells

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High Performing and Durable Pyrophosphate Based Composite Membranes for Intermediate Temperature Fuel Cells

2020 DOE Hydrogen and Fuel Cells
Program Review Presentation

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Overview

Timeline

- Project Start Date: January 2018
- Project End Date: July 2020

Budget

- Total Project Budget: \$300K
- Total Funds spent: \$226K (5/25/2020)

Barriers addressed

- Early stage membrane concept that can:
 - Decrease system costs by operating at higher temperature (150–400 °C)
 - Achieve membrane ASR of $\leq 0.02 \text{ } \Omega\text{cm}^2$
 - Achieve ASR $\leq 0.03 \text{ } \Omega\text{cm}^2$ under low RH conditions
 - Achieve sufficient conductivity ($0.2 \rightarrow 0.02 \text{ } \Omega\text{cm}^2$) across entire range of operating temperatures

Partners

- University of New Mexico (Prof. Fernando Garzon)
 - No cost partner

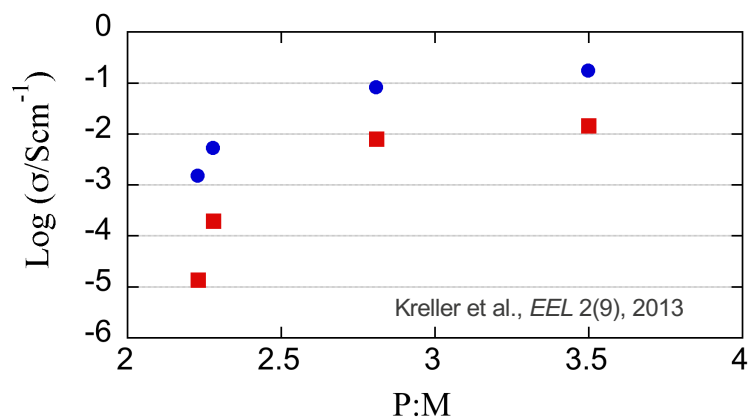
Relevance

Objectives:

- Develop metal pyrophosphate (MPP)/ Nafion composite membranes for operation at 200°C and low relative humidity (RH) for transportation applications
 - Optimize composition of MPP materials in order to achieve conductivities of 100 mScm⁻¹
 - Fabricate membranes of <40µm thickness in order to achieve membrane area specific resistance (ASR) of < 0.04 Ωcm²
 - Evaluate membrane durability in terms of crossover, shorting resistance, and open circuit voltage
-
- Fuel cells operating in the temperature regime of 150–400 °C would reduce system costs/ complexity
 - MPP/polymer composite membranes operate at 200 °C, <1% RH, and because they do not rely on phase change or high RH for H⁺ transport, they have the potential to extend operating range to lower temperatures during start-up
 - This membrane is at the initial stages of development with the potential to meet the following DOE membrane and MEA targets:
 - ASR: ≤0.02 Wcm²
 - ASR: ≤0.03 Wcm² under low RH conditions
 - Max hydrogen crossover: 2 mA/cm²
 - MEA performance: ≥300 mA/cm² @ 800 mV
 - MEA performance: ≥1000mA/cm² @ 675 mV

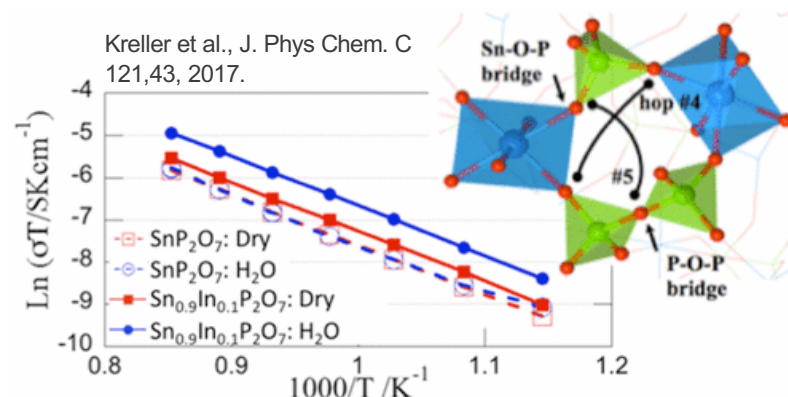
Approach: Motivation for MPP-based IT membranes

Conductivity at 250°C of $\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$ with excess amorphous polyphosphate phase (P:M>2)



Low Temp (<300°C) grain boundary conduction through excess polyphosphate phase

Conductivity at >600°C of $\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$, P:M=2

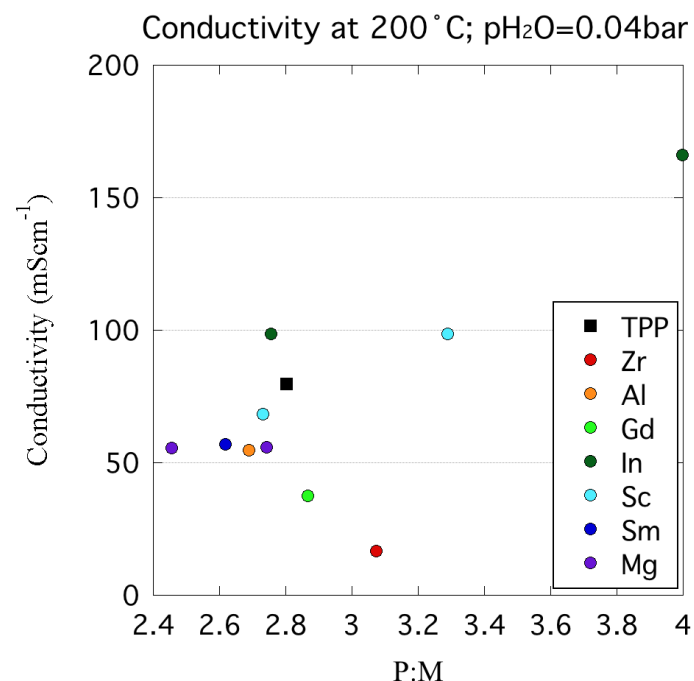
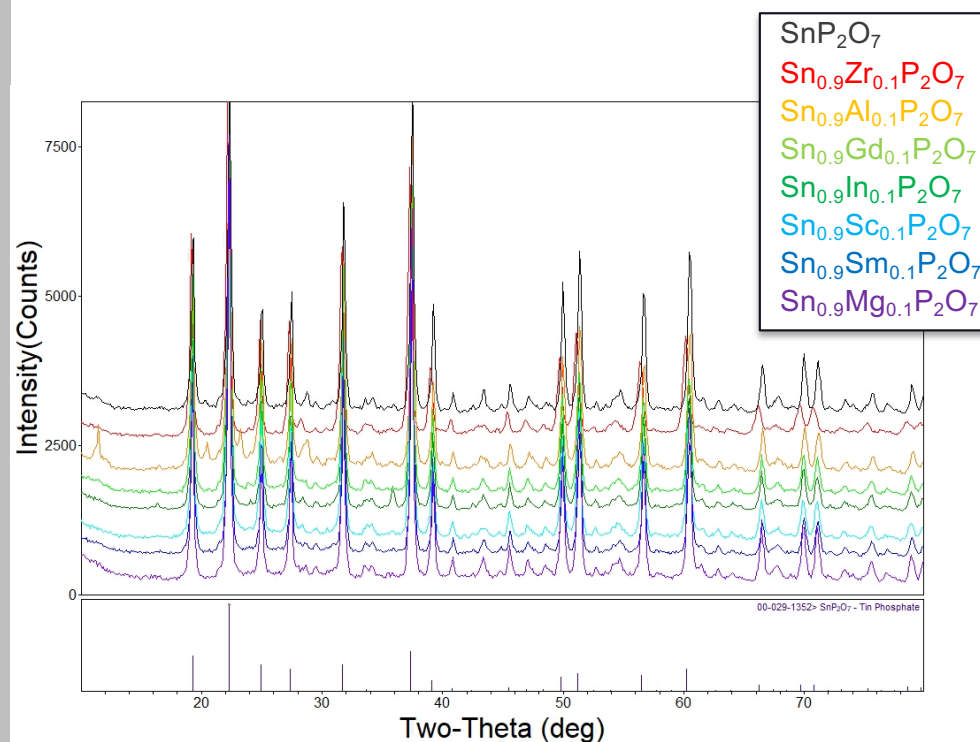


High Temp (>600°C) bulk crystalline hopping mechanism

- Initial publications on MP_2O_7 reported high conductivities at intermediate temperature and attributed this to a proton hopping mechanism through the bulk of the crystalline lattice.
- Our subsequent work found that the crystalline MP_2O_7 material exhibited negligible conductivity in the low-to-intermediate temperature range, and an amorphous grain boundary polyphosphate phase is required for IT proton conduction. This MP_2O_7 with excess phosphorous to metal ratio (P:M) exhibited high and stable operation at $T > 200^\circ\text{C}$.
- Multiple reports show MP_2O_7 conductivity at low-to-intermediate temperatures improved with introduction of lattice oxygen vacancies via aliovalent doping. We know that this is not a result of intragranular conduction. However matrix effect may be responsible for improving the intragranular conduction through the excess polyphosphate phase.

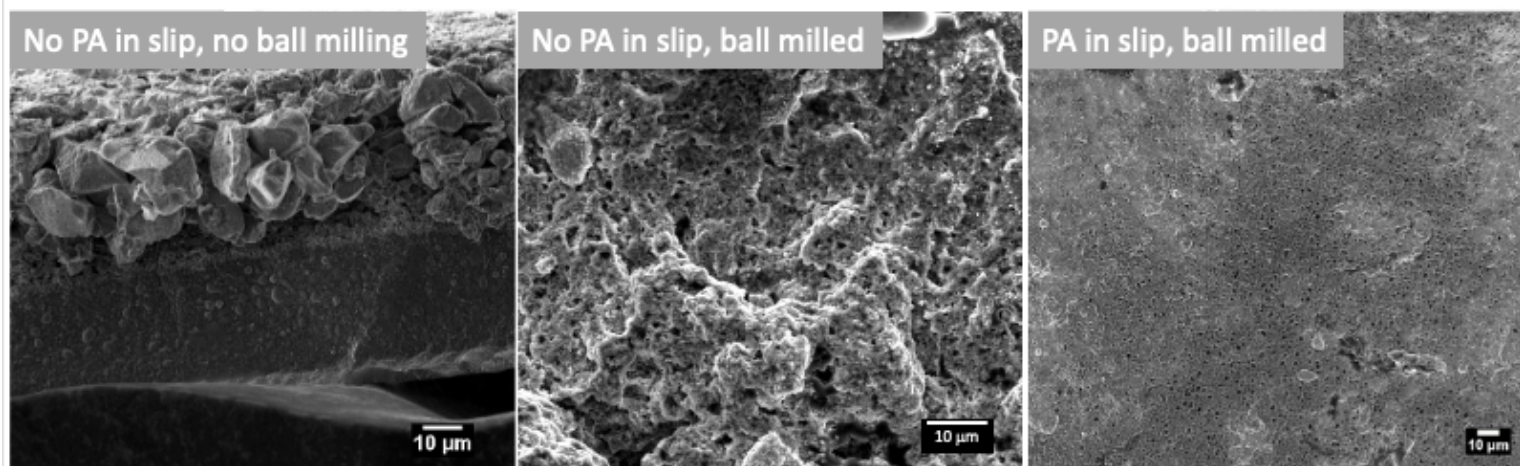
Approach: Optimizing composition of MPP

Various cation dopants were investigated and shown to have a pronounced effect on conductivity.



- Varying the dopant in $\text{Sn}_{(1-x)}\text{M}_{(x)}\text{P}_2\text{O}_7$ resulted in phase pure tin pyrophosphate structures for all dopants except Al
- As expected, conductivity increased with increasing P:M ratio
- Undoped SnP_2O_7 , $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$, and $\text{Sn}_{0.9}\text{Sc}_{0.1}\text{P}_2\text{O}_7$ exhibited the highest conductivities in bulk pellet form
- SnP_2O_7 (TPP) was used for membrane fabrication

Approach: Optimizing membrane fabrication



Initial membrane fabrication resulted in conductivities of $\sigma \sim 8 \text{ mS/cm}$ at 200°C that rapidly decreased with time resulting from 3 issues that have been addressed:

1. Large ceramic agglomerates
 - Ball milling the powder eliminated large ceramic particles/ agglomerates
 - Ball milling the powder did not greatly improve the dispersion of the components in the membrane- visible gaps in percolation of each phase identifiable in SEM
2. Porosity
 - Addition of phosphoric acid to slurry acted as plasticizer- improving particle dispersion and membrane quality
 - PA also greatly increased viscosity of slurry- sonication after ball milling introduced excess bubbles resulting in larger pores
 - Degassing at room temperature at vacuum chamber was used to remove bubbles from slurry prior to casting
3. Excess phosphate phase stability
 - Initial work substituting phosphoric acid for diammonium phosphate as the precursor for the TPP synthesis resulted in higher conductivities due to the removal of ammonium ions from the excess phosphate phase. However the conductivity of the TPP-PA decreased rapidly at 200°C
 - It was hypothesized that counter ion was necessary to stabilize excess phosphate phase. Bulk pellet conductivity varied with phosphate containing precursor. Precursor was found to have large large impact on ceramic particle size/ morphology and ultimately membrane density.

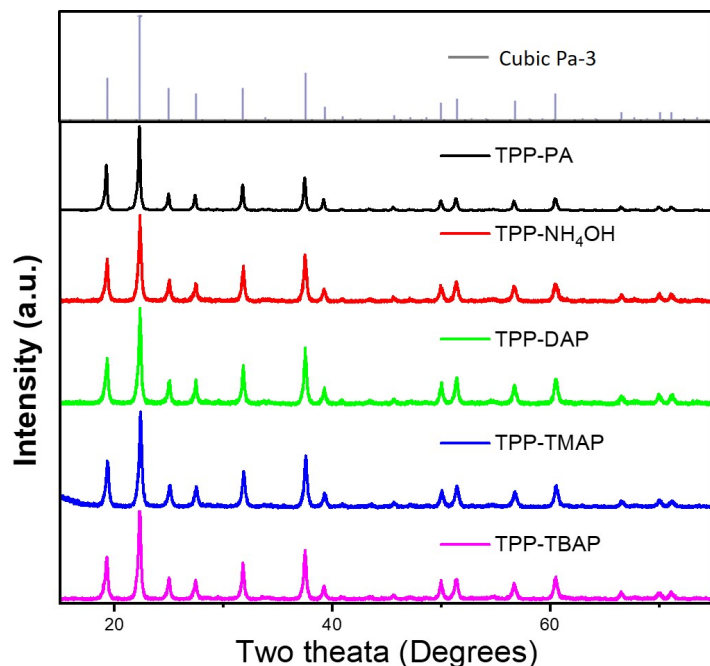
Accomplishments and Progress:

Preparation of TPP powders

Sample Name	Phosphate precursor	Sn precursor	Heating Process	Drying process
TPP-PA	85% phosphoric acid	SnSO_4 + Oxalic acid	Oxalic acid added and mixed at 80 °C under constant stirring	Dried at 140 °C overnight
TPP-NH ₄ OH	85% phosphoric acid + 30% NH ₄ OH	SnSO_4 + Oxalic acid	Oxalic acid added and mixed at 80 °C under constant stirring	Dried at 140 °C overnight
TPP-DAP	Diammonium phosphate	SnCl_4	Mixed at 60 °C under constant stirring	Dried at 80 °C overnight
TPP-TMAS	Tetramethylammonium sulphate + 85% Phosphoric acid	SnSO_4 + Oxalic acid	Oxalic acid added and mixed at 80 °C under constant stirring	Dried at 140 °C overnight
TPP-TBAP	Tetrabutylammonium phosphate	SnCl_4	Mixed at 80 °C under constant stirring	Freeze drying overnight.

- Following hypothesis that a counter ion was needed to stabilize the excess polyphosphate phase, varying phosphate precursors with varying counterion and molecular weight were investigated to improve TPP conductivity and optimize membrane performance

Accomplishments and Progress: Preparation of TPP powders

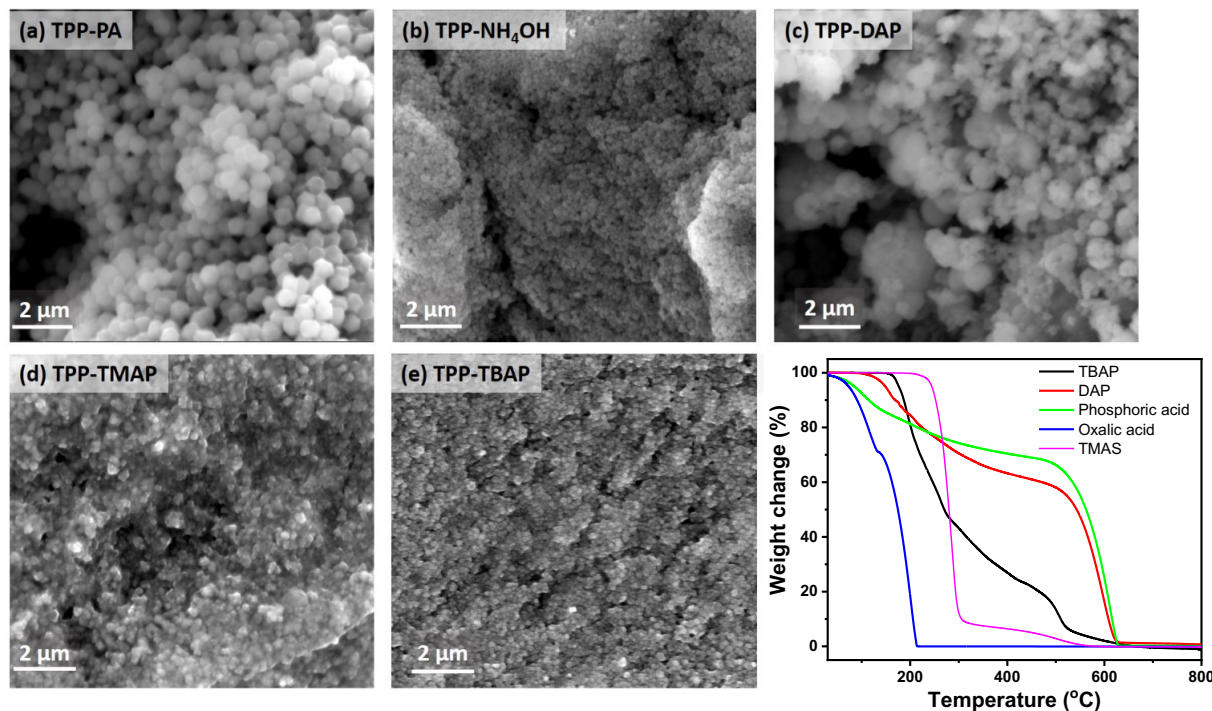


TPP powder	Crystallite size (nm)	Lattice Parameter (Å)	P:M ratio from TGA	Pellet conductivity (mS cm ⁻¹) @ 200 °C
TPP-PA	43.6	7.960	3.11	80
TPP-NH ₄ OH	29.1	7.948	3.08	76
TPP-DAP	32.4	7.948	3.16	67
TPP-TMAS	28.2	7.938	2.62	6
TPP-TBAP	30.1	7.947	3.02	88

- All precursors yielded the tin pyrophosphate crystalline structure
- Crystallite size obtained from whole profile refinement yielded similar size of ~30nm for all precursors except TPP-PA, which resulted in a crystallite size of ~44nm
- Synthesis yielded similar excess phosphate phase content as calculated by the mass loss in the TGA
- TPP-TMAS exhibited low and mixed-ionic electronic conductivity and was not studied further
- TPP-TBAP exhibited the highest conductivity

Accomplishments and Progress: Characterization of TPP powders

Varying precursors resulted in different particle size and morphology

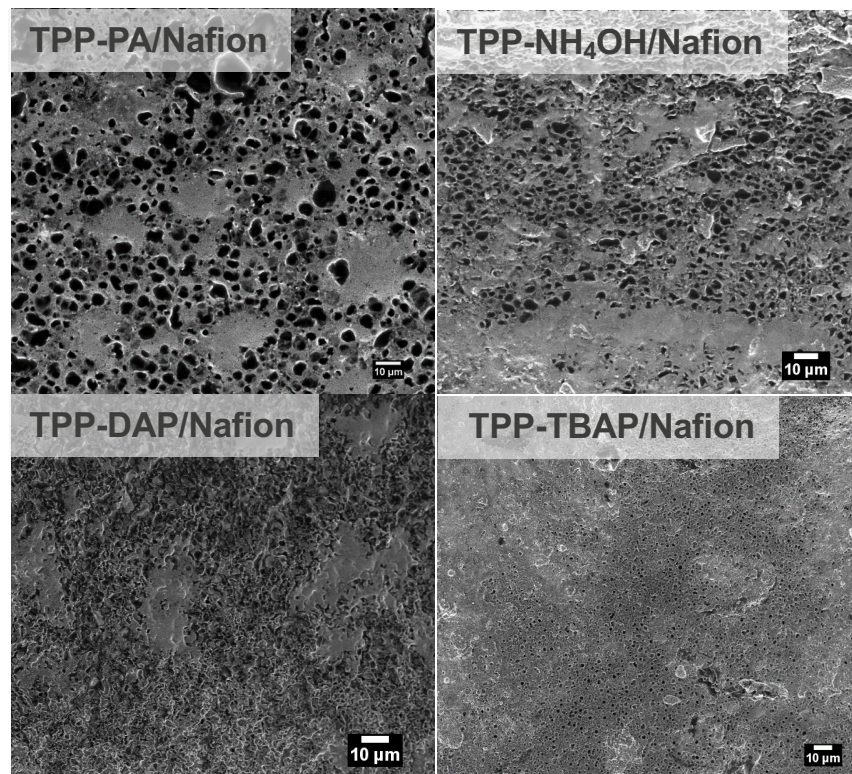


- TPP-PA formed ~500 nm particles. The addition of oxalic acid that has a low decomposition temperature (~200 °C) helped form well defined particles.
- TPP-DAP resulted in varying particle sizes of 200nm - 1μm, indicating that the addition of oxalic acid or inherent presence of hydrocarbon in the phosphate precursor (with decomposition at <400 °C) helps form well defined particles.
- TPP-TBAP, with a hydrocarbon content of ~67% and slow decomposition up to 500 °C, resulted in significantly smaller particles with average size of ~160 nm.
- TPP-NH₄OH and TPP-TMAP formed similar structural morphology with ~200nm particle sizes.
- The decomposition of the precursor in the temperature range 200 – 400°C is critical to uniform particle size with higher decomposition temperatures providing smaller TPP particle sizes.

Accomplishments and Progress:

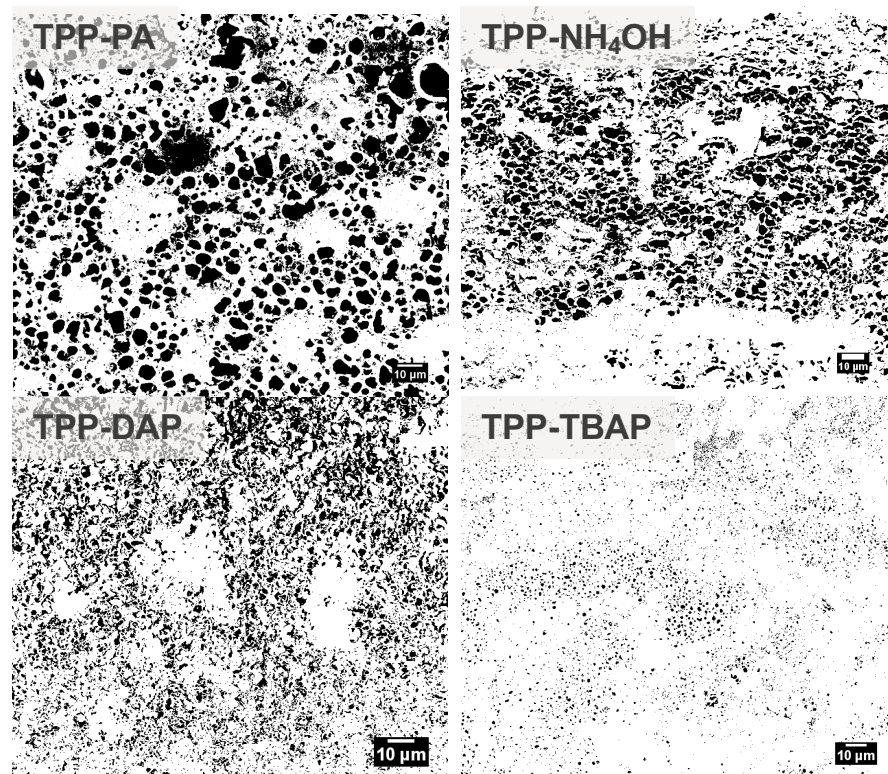
Characterization of membrane performance

SEM cross-sectional images



- Visible porosity in SEM images of the prepared membranes decreased with increasing cation size of ammonium ion precursor (or the resultant particle size):
TPP-PA < NH₄OH < DAP < TBAP
- TPP-TBAP exhibited lowest porosity as quantified by ImageJ analysis

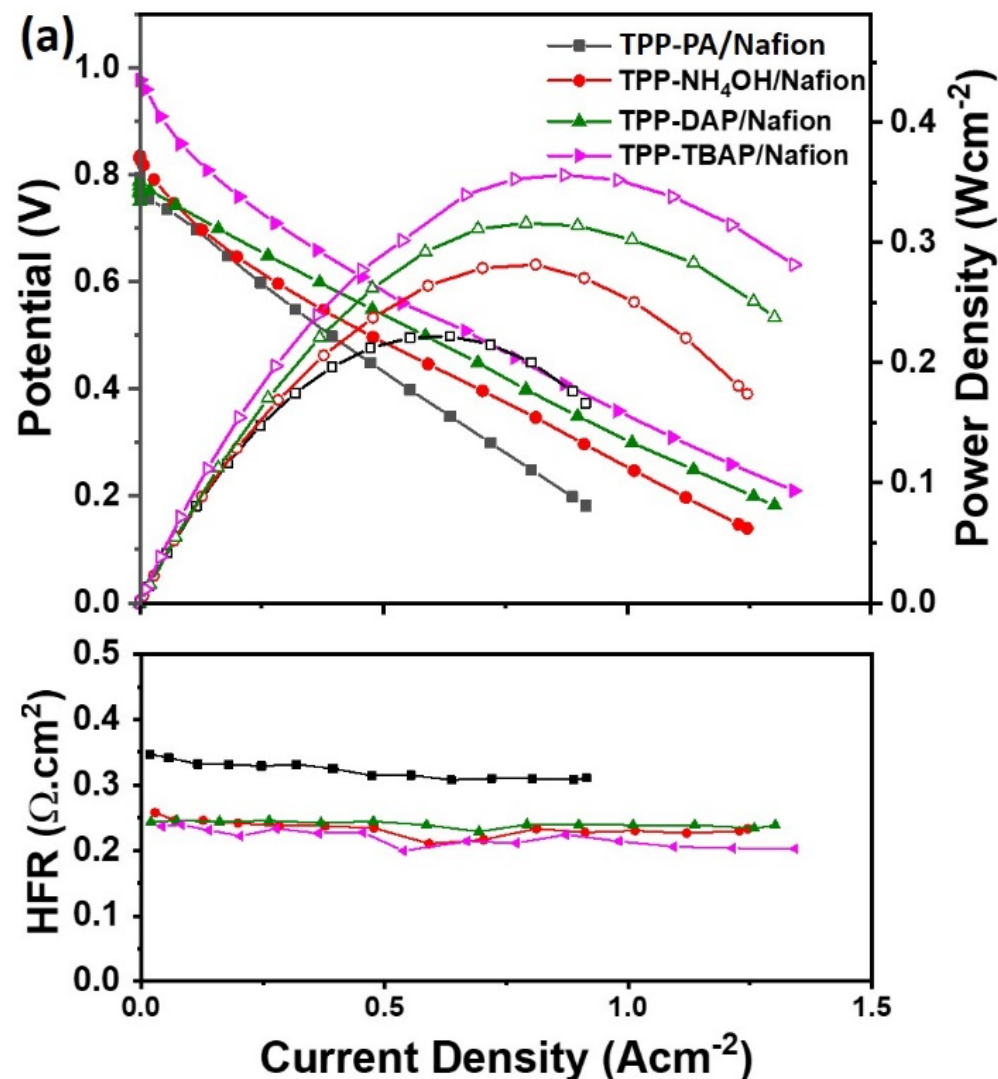
ImageJ porosity analysis



Membrane	Porosity, %
TPP-PA/ Nafion	35.3
TPP-NH ₄ OH/ Nafion	27.1
TPP-DAP/ Nafion	24.8
TPP-TBAP/ Nafion	4.2

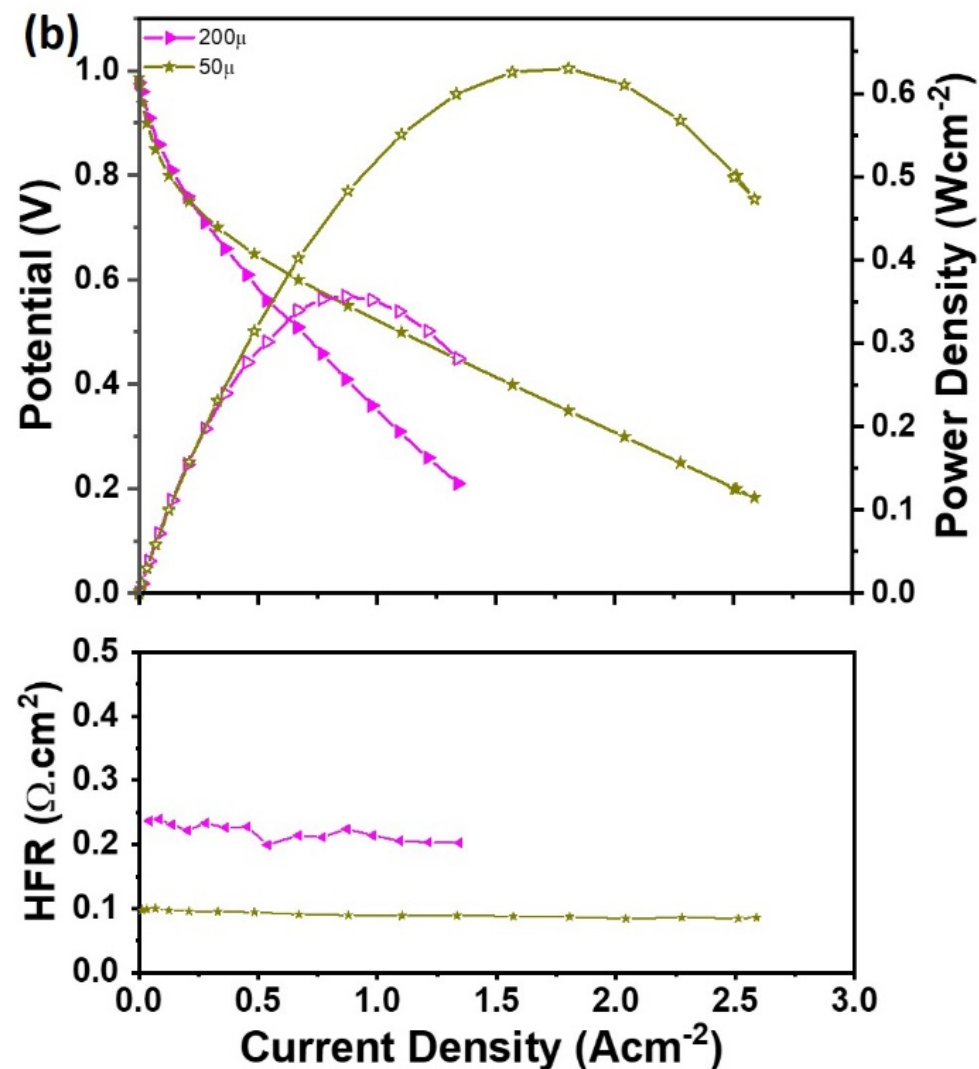
Accomplishments and Progress: Characterization of membrane performance

- Fuel cell performance based on 200 μm thick membranes varied depending on precursor used for TPP powder preparation
- TPP-PA powder exhibited lowest performance, lowest OCV and highest ASR
- Other precursors yielded similar ASR, but TPP-TBAP showed highest OCV and highest fuel cell performance owing to high density of membranes achieved with this formulation
- Achieved through-plane membrane conductivity of 95 mS cm^{-1} at 220°C and RH < 1% in a 5 cm^2 cell using a TPP-TBAP/Nafion composite membrane. (Y1 GNG 100 mS cm^{-1})**



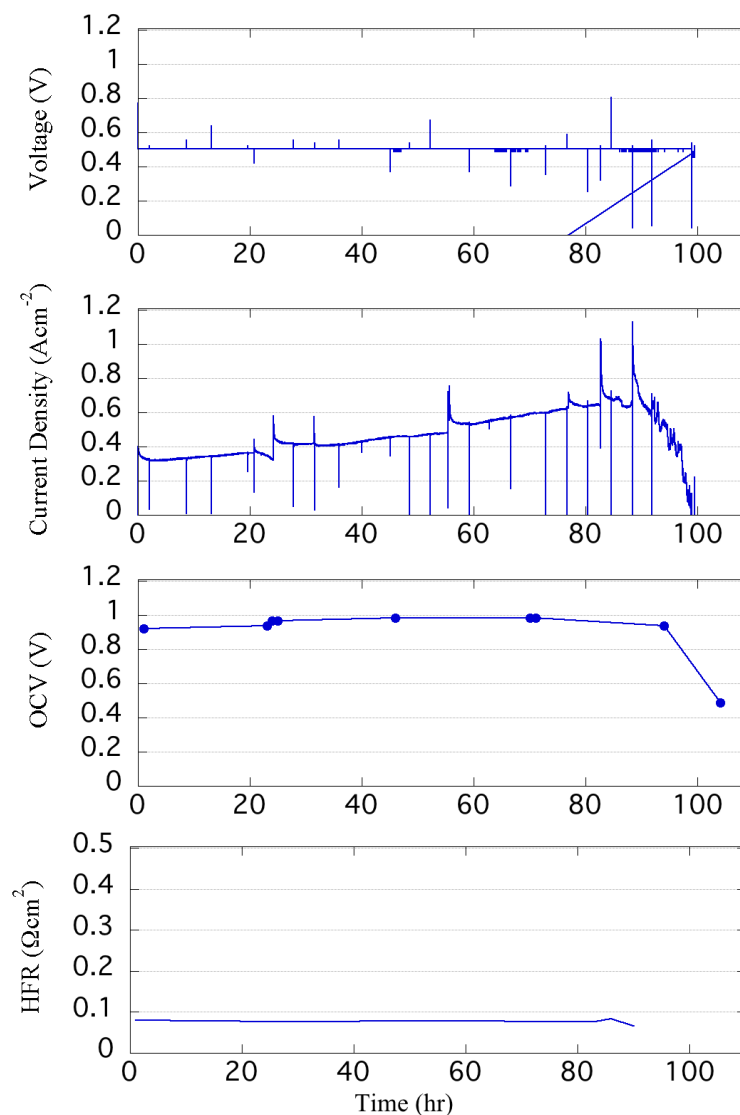
Accomplishments and Progress: Characterization of membrane performance

- Reducing TPP-TBAP membrane to 50 μm thickness decreased ASR to $0.1 \Omega\text{cm}^2$
- Power density increased from 355 to 630 mWcm^{-2}
- Maintained high OCV (0.98V) indicated high density retained upon reducing membrane thickness.



Accomplishments and Progress: Characterization of membrane durability

- Membrane: 50 μm TPP-TBAP
- Electrodes: 0.6 mgcm^{-2} Pt on carbon paper
- 100hr test run at 0.5V, 25psi back pressure in H_2/O_2
- Maintained high OCV up to 94 hours
- HFR constant at 0.08 Ωcm^2 for 80 hours, then increased and decreased slightly before failure
- Postmortem analysis of this membrane to understand failure mode is pending



Responses to Previous Year Reviewer's Comments

- ...project is behind schedule
 - We were behind on both time and money spent on this project due to external circumstances and were kindly granted a no-cost extension.
- ...the sulfonic acid moieties in Nafion (or another perfluorosulfonic acid [PFSA]) will start to degrade at 200°C, and the PFSA will flow significantly at more intermediate temperatures, such as 120°C and above. It is highly unlikely that such a composite membrane would survive hot and cool cycles without changing morphology
 - Valid concern. The polymer backbone should survive temperature cycling but the sulfonic acid moieties will degrade. In order to meet the goal of 0.2 Ωcm^2 at low temperatures our membranes will need to exhibit RT conductivities of 20mS/cm. Our current membranes exhibit conductivities of 10mS/cm at 50°C under dry conditions. Nafion conductivity is <5mS/cm under these conditions so we believe the conductivity is due to the composite. This value should increase as overall membrane conductivity is improved.
 - We will be testing membrane durability against hot and cool cycles in Y2:Q4.
- ...mechanical properties and permeation are missing and should be added to the characterizations to be conducted
 - Permeation measurements are included in Y2: Q3 and Q4 milestones

Collaboration & Coordination

- Lab call project open to National Labs only- no official collaborators
- University of New Mexico- no cost partner interested in evaluating membranes for fuel electrosynthesis reactors
- Will solicit more partners once proof of concept is established

Milestones

3/18	Synthesize and characterize 6 MPP materials with varying dopant concentration and P:M ratio	Met
6/18	Establish trends in conductivity with P:M ratio and cation dopant	Met
9/18	Fabricate membranes from MPP materials that exhibit high conductivities in powder form. Report membrane conductivities as a function of MPP loading and PA doping	Met
6/19	GNG: Demonstrate in-plane membrane conductivity of $\geq 100 \text{ mScm}^{-1}$ at $T > 200^\circ\text{C}$ and $\text{RH} < 0.04 \text{ bar}$ with a thickness $\leq 40 \text{ }\mu\text{m}$.	95 mScm^{-1}
9/19	Fabricate fuel cell that demonstrates through plane conductivity of $\geq 100 \text{ mScm}^{-1}$ at $T > 200^\circ\text{C}$ and $\text{RH} < 0.04 \text{ bar}$	95 mScm^{-1}
12/19	Demonstrate membrane ASR of $< 0.04 \text{ ohm cm}^2$ in a 5 cm^2 fuel cell	$.08 \text{ ohm cm}^2$
3/20	Achieve membrane durability (hydrogen crossover $< 15 \text{ mA/cm}^2$ shorting resistance $> 1000 \text{ }\Omega\cdot\text{cm}^2$, Open Circuit Voltage $> 0.9 \text{ V}$) for 100 hours under cyclic operation at $200\text{-}240^\circ\text{C}$	In progress
6/20	Achieve membrane durability for 1,000 hours	In progress

Proposed Future Work

- We have demonstrated conductivity of 95 mScm^{-1} at 220°C in a 5 cm^2 fuel cell using un-doped SnP_2O_7 and anticipate increasing to $>100 \text{ mScm}^{-1}$ by utilizing In-doped SnP_2O_7 and increasing the P:M ratio of the MPP material.
- We will try to reduce the ASR from 0.08 to $<0.04 \text{ } \Omega\text{cm}^2$ by reducing the thickness of the membrane to $40 \text{ } \mu\text{m}$ using the MPP material with the highest conductivity.
- Durability will be evaluated against DOE technical targets for hydrogen crossover, shorting resistance and open circuit voltage.
- Durability over temperature cycling will also be evaluated.

Summary

Objective:	Develop a novel proton conducting electrolyte operating at $>200^{\circ}\text{C}$ with conductivity $\sigma \geq 100 \text{ mS cm}^{-1}$ and $\text{RH} < 1\%$. Fabrication of membranes of less than $40\mu\text{m}$ thickness while retaining high conductivity will result in $\text{ASR} < 0.04 \Omega\text{cm}^2$. Evaluate membrane durability in terms of crossover, shorting resistance, and open circuit voltage, as well as against temperature cycling.
Relevance:	Operating FCs in the intermediate temperature range has the potential to greatly reduce cost and simplify water and thermal management. This effort requires novel materials and approaches to meet DOE membrane performance and durability targets. MPP/Polymer composite membranes show promise in early development for application in IT-FCs for transportation applications.
Approach:	We have demonstrated that both cation dopants and phosphate precursor influence MPP conductivity and identified the most promising MPP compositions for membrane fabrication. The ceramic MPP materials are fabricated as a composite membrane in a 90:10 wt% ratio with Nafion. We have modified our membrane fabrication procedure to improve the density of our membranes.
Accomplishments:	We demonstrated through-plane membrane conductivity of 95 mS cm^{-1} at $T > 200^{\circ}\text{C}$ and $\text{RH} < 0.04\text{bar}$ with a thickness $50\mu\text{m}$. We demonstrated FC performance up to 94hrs at 220°C and $< 1\% \text{ RH}$ with a $50\mu\text{m}$ thick membrane exhibiting an OCV of 0.98V and ASR of $0.08 \Omega\text{cm}^2$.
Future work:	Further decrease in ASR is expected by decreasing the membrane thickness to $< 40\mu\text{m}$. ITPP with higher P:M ratio will be used to increase the conductivity of the starting material. Long term durability will be assessed against DOE technical targets

Technical Back-up Slides

Accomplishments and Progress: Characterization of membrane durability

- Polarization curves associated with 100hr durability test
- Performance increase observed over time likely due to cell break in period

